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**COMPREHENSIVE CHEMICAL ANALYSIS
OF METAL ALLOYS BY MEANS OF
INDUCTIVELY COUPLED PLASMA
OPTICAL EMISSION SPECTROSCOPY**

W. E. Glad

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**Naval Ocean Systems Center**

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EXECUTIVE SUMMARY

PROBLEM

Extend the analysis capability of inductively coupled plasma (ICP) optical emission spectroscopy to as many different copper, aluminum, and iron base alloys as possible, and investigate the development of analytical methods capable of determining all important elements in a particular base through the use of a single set of analytical lines and a single sample preparation method.

RESULTS

Analyses of standard reference materials show that the analysis lines used were effective for determining those elements which can be brought into solution, particularly copper, chromium, cobalt, manganese, molybdenum, silicon, vanadium, and phosphorous. Other materials, notably aluminum, boron, titanium, tantalum, niobium, tungsten, and zirconium in an iron base were more difficult to analyze, probably because they form carbides or other species that are difficult to dissolve. The uses of NaOH/H₂O₂ to dissolve aluminum base material and HCl/H₂O₂ to dissolve copper base material show promise as good comprehensive dissolution techniques. The conductive solids nebulizer (CSN) proved effective in bypassing the dissolution step.

RECOMMENDATIONS

Additional research is needed on the dissolution of steels, particularly methods that release the carbide-forming elements from steel. Research should continue into the CSN's capabilities in bypassing the dissolution step, in particular its effectiveness on more highly alloyed material. If it is possible to use a single solid sample to readjust the calibration curves by means of the CSN, it may also be possible to analyze a wide variety of different alloys without purchasing a large number of expensive solid standards.

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CONTENTS

INTRODUCTION	page 1
EXPERIMENTS	1
SPECTROMETER	1
CHEMICALS	2
CALIBRATION	2
SAMPLE PREPARATION	2
RESULTS AND DISCUSSION	3
CONCLUSIONS	21
REFERENCES	22

TABLES

1.	Multielement standards	page	4
2.	Wavelengths		5
3.	Analytical line choices		11
4.	Interference corrections		14
5.	Results for iron base standards		15
6.	Results for aluminum base standards		18
7.	Results for copper base standards		18
8.	Ratio of liquid calibration slopes to CSN slopes		20

FIGURES

1.	Wavelength scans around the S-180 line	page	13
2.	Calibration curve for nickel with CSN-ICP		19
3.	Calibration curve for magnesium with CSN-ICP		21

INTRODUCTION

In recent years, chemical analysis by means of inductively coupled plasma (ICP) optical emission spectroscopy has become increasingly popular. This popularity has resulted from several favorable properties of ICP, among the most important being multielement analysis capability, good sensitivity, and a large linear dynamic range. While it has been demonstrated that ICP can be used to analyze some metal alloys for some elements with reasonable success (ref 1, 2), standard methods for ICP analysis of metal alloys do not exist. The purpose of this work is to extend the analysis capability of ICP to as many different copper, aluminum, and iron base alloys as possible, with an eye towards the development of analytical methods capable of determining all important elements in a particular base through the use of a single set of analytical lines and a single sample preparation method.

Efficient, sequentially scanning ICP spectrometers now make it possible to choose the best line in the atomic spectrum of an element for determining the concentration of that element in any given sample matrix without unreasonably degrading the speed of analysis. The line choice must be made with care to avoid spectral interferences from the matrix element and any major alloying elements. Line choices for aluminum, iron, and copper base materials are given here.

One drawback of the ICP is that it requires the sample to be in solution. The multielement capability of the ICP makes it desirable to use sample preparation methods that simultaneously release as many elements as possible into solution. Often it is impossible to find a sample dissolution method that will release all constituents of a sample simultaneously. A few sample dissolution procedures are investigated here. The usefulness of both the sample dissolution procedure and the analytical line choice will be tested by analyzing some certified reference materials with ICP.

In addition, some preliminary investigations with a conductive solids nebulizer (CSN) are discussed. The CSN introduces material into the plasma as an aerosol eroded from the surface of the sample by a medium voltage spark, thus avoiding the dissolution step.

EXPERIMENTS

SPECTROMETER

The spectrometer used was an Applied Research Laboratories 3580. The spectrometer configuration consists of a 45-channel polychromator and a separate scanning monochromator. Both the polychromator and monochromator contain 1080-line/mm gratings as the dispersive element. The gratings can be used in the first through fourth spectral orders. Most spectral lines are chosen in the second or third spectral orders. The effective resolution is 0.028 nm in the second order and 0.019 nm in the third order. The resolution calculation assumes a 50 μm secondary slit width. The secondary slit width in the monochromator is 50 μm . Most secondary slits in the polychromator are also 50 μm wide, but a few are 75 μm or 37 μm wide, which would result in a respectively poorer or greater resolution, depending on the respective width.

The plasma torch was operated with 1200 watts incident power, and with the observation height 15 mm above the load coil. The nebulizer for liquids work was of the pneumatic concentric type. The sample uptake rate was about 2.5 ml/minute with this nebulizer.

The conductive solids nebulizer was also manufactured by Applied Research Laboratories. The CSN consists of a spark source and a standard spark analysis table. Argon gas passes through the table and sweeps aerosol generated by the spark discharge through a 1-meter piece of 1/4-inch plastic tubing into the plasma torch. The tubing is connected to the torch, where the liquid sample spray chamber is normally connected. Normal operating procedure with the CSN is to first flush the system with a 12-liter/min flow of argon for 5 seconds, then prespark the sample with a 5-liter/min gas flow for 20 seconds. After presparking, the sparking conditions are changed and the gas flow is reduced to 1 liter/min while signals are integrated. Prespark conditions for the 120-Hz spark discharge are 500 V, with 10 μ F of capacitance and 12 μ H of inductance in the circuit. For aluminum base materials, the prespark voltage is reduced to 350 V. During integration, 2.2 Ω and 100 μ H are added to the circuit and the voltage is reduced to 400 V for iron and maintained at 350 V for aluminum.

CHEMICALS

Multielement standard solutions were prepared from commercially available atomic absorption standard solutions or Spex Industries plasma-grade materials. Samples were dissolved with J.T. Baker Ultrex-grade acids and sodium hydroxide solution made from reagent-grade sodium hydroxide. Reagent-grade hydrogen peroxide was also used in the dissolution of some samples.

CALIBRATION

Calibrations were generated by using the multielement standards described in table 1. Most calibration data were fit to linear curves. Nickel and chromium in steel, and copper in copper base materials, all of which showed slight deviations from linearity at high concentrations, were fitted to second-order polynomials.

SAMPLE PREPARATION

Samples of copper base material (0.5 g) were accurately weighed and dissolved by adding 5 ml of deionized water and 5 ml of concentrated nitric acid in a 50-ml Teflon beaker. After the reaction subsided, heat (below boiling) was applied from a hot plate to complete dissolution. Alternately, copper base samples were dissolved by using 5 ml of concentrated hydrochloric acid as well as sufficient hydrogen peroxide and slow heating to complete dissolution. Samples were diluted to 100.0 ml with deionized water.

To dissolve aluminum-base material, 5 ml of 20% NaOH solution was added to samples (0.20 g) in a Teflon beaker. After the reaction subsided, slow heating was begun and sufficient hydrogen peroxide was added to dissolve silicon. (This treatment also oxidizes most copper, but it remains precipitated in the strongly basic solution.)

Solutions were acidified by adding 5 ml of concentrated HCl. Any remaining unoxidized copper can be dissolved at this time by adding a little more hydrogen peroxide. This treatment sometimes leaves manganese undissolved as MnO_2 . The MnO_2 can be reduced to soluble Mn^{2+} by the addition of a small amount of Na_2SO_3 . Samples were diluted to 100.0 ml with deionized water.

Low-alloy and carbon steels were dissolved by the addition of 5 ml of deionized water and 5 ml of concentrated nitric acid to the sample (0.5 g) in a Teflon beaker. Samples were heated below boiling for 20 minutes to dissolve as much carbon as possible. Five ml of hydrochloric acid was then added to the samples and heating continued for another 20 minutes. Stainless steels were dissolved by adding the hydrochloric and nitric acids together at the start, since these steels are somewhat resistant to nitric acid alone. Samples were diluted to 100.0 ml with deionized water.

RESULTS AND DISCUSSION

A number of atomic emission lines were examined with the ICP for sensitivity and spectral interferences. Table 2 gives the wavelengths of the lines, their detection limits, and the wavelengths of important interfering lines. Detection limits were determined by making 11 measurements of a deionized water blank to determine its reproducibility (standard deviation). An appropriate high standard of the element of interest was then measured to complete a two-point calibration curve. The detection limit quoted in table 1 is defined as the concentration of the element required to produce a signal equal to twice the standard deviation of the blank. The detection limits refer to 5-second integrations in all cases. The detection limits for a number of lines in the vacuum ultraviolet are lower than expected because of optical degradation peculiar to this spectrometer. Other instruments could expect sensitivity as large as 10 times greater for some of these lines.

Interferences were detected by scanning the wavelength in the vicinity of the spectral line of interest while a solution of the suspected interfering species was aspirated into the plasma. Solutions of 4000-ppm iron, 1000-ppm aluminum, 100-ppm manganese, 200-ppm zinc, 200-ppm chromium, 200-ppm tungsten, 200-ppm copper, 100-ppm silicon, 500-ppm nickel, 500-ppm tin, and 200-ppm molybdenum were examined as potentially interfering species. A region 0.1 nm on either side of the line of interest was scanned. Even though some of the interfering lines listed in table 2 are outside of the spectral bandpass of the target line, it is important to note their presence since the spectral background is usually measured within 0.1 nm of the analytical line during the analysis sequence. Background measurement is important because differences between the calibration matrix and the sample matrix may cause small baseline shifts that can affect the accuracy of determining trace elements. Measuring the off-peak background during analysis can account for these baseline shifts. It is important to measure background away from any interfering lines, since an interference on the background measurement will produce a negative concentration error.

After consideration of the sensitivity and interference data, analytical lines were chosen for aluminum, iron, and copper base material. The lines chosen are given in table 3. Also shown is the wavelength at which spectral background for the line is

Table 1. Multielement standards.

Standards for Iron Base

Blank	5% HNO ₃ , 5% HCl
Standard 1	5% HNO ₃ , 5% HCl, 5 Co, 10 Cr, 5 Cu, 5 Mo, 2500 Fe, 10 Mn, 10 Si
Standard 2	5% HNO ₃ , 5% HCl, 5 B, 50 Co, 250 Cr, 10 P, 20 Ti, 10 S
Standard 3	5% HNO ₃ , 5% HCl, 50 Al, 50 Cu, 250 Ni, 20 V, 100 Mn, 100 Si, 5000 Fe
Standard 4	5% HNO ₃ , 5% HCl, 10 As, 100 Mo, 20 Nb, 10 Pb, 20 Sn, 20 Ta, 20 W, 20 Zr, 5000 Fe
Standard 5	5% HNO ₃ , 5% HCl, 1500 Cr, 250 Cu, 1500 Ni, 3000 Fe

Standards for Aluminum Base

Blank	5% HCl, 5% of the NaOH solution
Standard 1	5% HCl, 5% of the NaOH solution, 1 Be, 10 Cu, 10 Mg, 10 Si, 10 Zn, 2000 Al
Standard 2	5% HCl, 5% of the NaOH solution, 20 Bi, 10 Cd, 10 Pb, 10 Sn, 2000 Al
Standard 3	5% HCl, 5% of the NaOH solution, 5 B, 10 Be, 10 Cr, 100 Cu, 100 Mg, 50 Mn, 10 Ni, 200 Si, 5 Sr, 10 Ti, 150 Zn, 20 Fe, 2000 Al

Standards for Copper Base

Blank	5% HNO ₃
Standard 1	5% HNO ₃ , 100 Al, 20 Fe, 100 Sn, 100 Zn, 50 P, 10 As, 10 S, 20 Sb, 20 Si, 20 Pb, 5000 Cu
Standard 2	5% HNO ₃ , 100 Ni, 100 Mn, 5000 Cu
Standard 3	5% HNO ₃ , 2500 Cu, 2500 Ni, 500 Sn
Standard 4	5% HNO ₃ , 2500 Cu, 2500 Zn

Table 2. Wavelengths.

Element	Wavelength	DL(ppm)	Interfering Element	Interfering Wavelength
Ag	338.29	0.006	W	338.23
			W	338.31
			Fe	338.22
			Mo	338.22
			Cr	338.33
Ag	328.068	0.003	Cu	327.98
			Fe	328.025
			Fe	328.13
Al	394.40	0.02		
Al	308.215	0.13	Mn	308.27
Al	167.081	0.22	Mo	308.21
			W	167.04
			Fe	167.07
			Cr	167.04
			Fe	167.04
Al	396.152	0.02	Fe	396.10
As	189.042	0.56	Mo	396.14
			Fe	188.98
			Fe	189.11
			Mo	189.01
			Mo	189.08
As	193.76	0.79	W	193.82
As	197.262	2.6	Fe	193.72
			W	197.33
As	234.984	0.59	Fe	197.21
			W	234.98
			W	234.92
			W	235.04
			Fe	Wing
B	182.590	0.006	Mn	182.63
B	249.680	0.004	Fe	249.73
			Fe	249.623
			Mo	249.728
			Mo	249.610
Be	313.042	0.0004		
Be	234.861	0.0013	Fe	234.82
			Mo	234.89
Bi	306.70	0.49	Fe	306.75
Bi	223.061	0.18	W	223.12
			Zn	223.03
			Cu	223.01
			Fe	223.13
			Mo	223.01

Table 2. Wavelengths. (Continued)

Element	Wavelength	DL(ppm)	Interfering Element	Interfering Wavelength
Ca	319.33	0.01	W	317.90
			W	317.93
			W	318.00
			Mn	317.93
			Mn	318.00
			Mn	317.84
			Fe	317.95
			Fe	318.02
			Fe	393.36
Ca	393.366	0.0002	Fe	422.75
Ca	422.673	0.035	Fe	228.75
Cd	228.802	0.007	W	214.41
Cd	214.438	0.02	Fe	214.39
			Fe	214.45
			Fe	214.47
			Cr	214.485
			W	226.54
Cd	226.502	0.01	Fe	226.45
			Fe	226.50
			Al	Wing
			Al	Wing
Co	228.620	0.015		
Co	258.030	0.027		
Co	237.848	0.04		
Cr	267.72	0.03	W	267.727
			Mn	267.725
Cr	205.552	0.31	Cu	205.457
			Fe	205.50
			Fe	205.59
			Al	Wing
			Si	205.54
			Zn	206.19
Cr	206.149	0.47	Mo	206.12
			Al	206.17
			Al	206.17
Cu	327.400	0.0041		
Cu	224.70	0.0275	W	224.66
			Fe	224.69
			Fe	224.76
			Fe	324.71
Cu	324.754	0.0024	Fe	324.83
Ga	417.20	0.05	Fe	417.217
			Fe	417.217

Table 2. Wavelengths. (Continued)

Element	Wavelength	DL(ppm)	Interfering Element	Interfering Wavelength
Ga	294.364	0.04	W	294.44
			Mn	294.31
			Mn	294.39
			Fe	294.46
			Mo	294.33
			Mo	294.41
Mg	279.08	0.02		
Mg	279.553	0.002	Mn	279.48
			Mn	279.52
			Mn	279.61
			Fe	279.55
			Fe	279.583
			Cr	279.583
Mn	293.306	0.006	Cr	293.27
			Mo	293.32
			W	293.29
Mn	257.610	0.001	Al	257.68
			Fe	257.68
			Fe	257.57
			Cr	257.58
			W	257.63
			Mo	257.66
			Mo	257.58
			Fe	257.58
			Fe	294.92
Mn	294.92	0.015		
Mn	259.370	0.002		
Mo	202.03	0.009	W	201.955
			W	201.984
			Fe	201.989
			Cr	201.989
			Mn	281.64
			Cr	281.69
Mo	281.615	0.046		
Mo	203.85	0.42		
Nb	319.5	0.04	Fe	203.82
			Fe	203.82
Nb	309.417	0.05	W	309.36
			Fe	309.38
			Mo	309.47
			Cr	309.47
			Cr	309.347
			Cr	309.396
Nb	316.340	0.026	W	316.34
			Fe	316.31
			Cr	316.38
Ni	231.604	0.013	Cr	316.38
			Mn	231.595

Table 2. Wavelengths. (Continued)

Element	Wavelength	DL(ppm)	Interfering Element	Interfering Wavelength
Ni	221.647	0.03	W	221.62
			W	221.60
			Fe	221.64
			Fe	221.70
			Cr	221.60
			Si	221.65
Ni	227.021	0.075	W	227.02
			Mo	226.97
			Al	Wing
P	178.287	0.08	W	178.32
			Mn	178.275
			Mo	178.267
P	177.50	0.50	Fe	177.47
			Fe	177.52
			Cr	177.50
P	255.328	4.6		
P	214.914	1.2	Fe	214.91
Pb	405.78	0.44		
Pb	216.999	0.68	W	216.95
			W	217.00
			Cu	216.95
			Fe	217.00
			Fe	217.05
			Fe	216.95
			Mo	216.95
			Mo	217.01
			W	220.41
			W	220.46
			Fe	220.34
Pb	220.353	0.04	Fe	220.42
			Fe	220.40
			Al	Wing
			W	283.36
			Fe	283.24
			Fe	283.31
			Fe	283.40
S	180.731	0.07	Mn	180.719
			Mn	180.743
			Cr	180.736
			W	182.03
S	182.037	0.25	Fe	181.98
				182.10
			Fe	259.94
Sb	259.81	0.17		

Table 2. Wavelengths. (Continued)

Element	Wavelength	DL(ppm)	Interfering Element	Interfering Wavelength
Sb	187.115	1.2	W	187.11
			Mn	187.06
Sb	217.581	0.29	W	217.54
			W	217.56
			W	217.64
			Fe	217.54
			Fe	217.69
			Fe	217.65
Sb	231.147	0.33	Fe	231.12
			Fe	231.20
Si	212.41	0.07	Cu	212.41
			Mo	212.412
Si	288.16	0.10	Cr	288.206
			Mo	288.128
			Mn	288.094
			W	288.16
Sn	317.50	0.39		
Sn	189.98	0.25	W	189.91
			W	190.04
			Fe	189.99
			Mo	189.93
			Cr	190.04
Sn	242.949	0.27	W	242.94
			Fe	242.94
			Fe	243.01
			Mo	242.91
Sr	346.446	0.01	Fe	346.41
			Fe	346.57
Sr	421.55	0.0014	Fe	421.54
			Fe	421.62
Sr	407.771	0.0003	Fe	407.84
Ta	240.00	0.09	Fe	239.94
Ta	226.23	0.15	Fe	226.27
Ta	268.517	0.023	Mn	268.45
			Mn	268.59
			Fe	268.48
			Cr	268.51
Ti	342.20	0.01	W	
Ti	308.80	0.003	Mo	308.76
Ti	336.12	0.005	W	336.11
			Mo	
			Cr	336.03
			Cr	336.18

Table 2. Wavelengths. (Continued)

Element	Wavelength	DL(ppm)	Interfering Element	Interfering Wavelength
Ti	337.28	0.003	Mo	337.30
			Fe	337.28
			Fe	337.21
V	311.07	0.002	Mn	311.061
			Fe	311.094
			Mo	311.088
			Ti	311.072
V	290.881	0.008	Mn	290.88
			Zn	290.86
			Fe	290.88
			Fe	290.95
			Mo	290.92
			Cr	290.91
			W	292.34
			W	292.55
V	292.402	0.003	Fe	292.38
			Mo	292.33
			Mo	292.44
W	209.86	0.14		
W	220.45	0.05		
W	207.911	0.96	Cr	207.90
W	239.709	0.58	Fe	239.66
Zn	202.551	0.065	W	202.61
			Fe	202.49
			Cr	202.56
			Cu	202.55
			Cr	206.14
			Al	206.163
Zn	206.191	0.47		
Zn	213.856	0.01	W	213.82
			Cu	213.85
			Fe	213.86
			Fe	213.88
			Fe	213.80
Zr	349.62	0.018	Mn	349.56
Zr	339.198	0.008	Fe	339.21
			Fe	339.23
			Fe	339.24
			Mo	339.18
Zr	343.823	0.003	Mn	343.90
			Fe	343.79
			Fe	343.83

Table 3. Analytical line choices.

IRON BASE

Element	Wavelength (nm)	Background Wavelength (nm)	Spectral Bandpass (nm)
Al	308.215	308.275	0.028
As	189.042	189.002	0.019
B	182.590	182.550	0.019
Co	228.620	228.580	0.026
Cr	267.720	267.680	0.026
Cu	327.400	327.339	0.028
Mn	293.306	293.339	0.028
Mo	202.030	202.059	0.019
Nb	319.500	319.561	0.028
Ni	231.600	231.560	0.026
P	178.290	178.330	0.019
S	180.730	180.687	0.019
Se	196.090	196.040	0.019
Si	212.410	212.471	0.028
Sn	189.980	189.884	0.019
Ta	240.060	240.124	0.015
Ti	336.121	336.191	0.028
V	311.070	311.131	0.028
W	220.450	220.413	0.019
Zr	349.620	349.681	0.029

ALUMINUM BASE

Element	Wavelength (nm)	Background Wavelength (nm)	Spectral Bandpass (nm)
B	249.680	249.640	0.019
Be	313.040	312.979	0.028
Bi	223.061	223.151	0.028
Cd	228.800	228.739	0.039
Cr	267.720	267.680	0.026
Cu	324.754	324.664	0.028
Fe	259.940	260.110	0.028
Ga	294.364	294.314	0.028
Mg	279.080	279.010	0.028
Mn	259.370	259.440	0.028
Ni	231.600	231.560	0.026
Pb	283.310	283.351	0.028
Sb	259.810	259.749	0.015
Si	288.160	288.099	0.039

Table 3. Analytical line choices. (Continued)

Element	Wavelength (nm)	Background Wavelength (nm)	Spectral Bandpass (nm)
Sn	189.980	190.070	0.019
Sr	407.771	407.881	0.055
Ti	337.280	337.180	0.028
Zn	213.856	213.916	0.019

COPPER BASE

Element	Wavelength (nm)	Background Wavelength(nm)	Spectral Bandpass (nm)
Cu	224.260	--	0.026
Al	308.215	308.275	0.028
As	189.042	188.992	0.019
Mn	257.610	257.560	0.028
Ni	231.600	231.560	0.026
P	178.290	178.250	0.019
Pb	220.353	220.423	0.019
Sn	189.980	190.070	0.019
Fe	259.940	260.010	0.028
S	180.730	180.690	0.019
Sb	217.581	217.651	0.019
Si	288.160	288.099	0.039
Zn	206.191	206.261	0.019

measured, as well as the effective spectral bandpass (half width at half maximum) for the line. Some of the lines chosen for analysis have unavoidable interferences. Correction coefficients for these interferences were measured and are tabulated in table 4. Because ICP calibration curves are usually linear, corrections can be made simply by subtracting, from the apparent concentration, a concentration proportional to the concentration of the interfering species.

Thirteen iron base National Bureau of Standards standard reference materials were dissolved and analyzed. Table 5 compares the results obtained with the certified values. Very good accuracy was shown for copper, chromium, cobalt, manganese, molybdenum, silicon, vanadium, and phosphorus. The results for arsenic and sulfur were not as accurate, but are probably adequate for most analytical work. The arsenic results simply suffer from poor sensitivity. The sensitivity for sulfur is adequate, but because sulfur is determined at such low levels in most steels, interferences can cause a degradation of precision even when they are correctable. This is because the signal from the interfering species can exceed the signal from sulfur itself. Initially observed poor accuracy for sulfur in stainless steel was partially explainable by the fact that chromium at the high levels normally found in stainless steels interferes with the sulfur line. Figure 1 shows a wavelength scan of 5000-ppm chromium in the vicinity of the sulfur line, a wavelength scan over the same region of a 24% chromium stainless steel, and a wavelength scan of 2-ppm sulfur in deionized water. Note that 4 ppm of sulfur would correspond to 0.08% sulfur in a steel sample under the dilution conditions used here. Figure 1 illustrates the problem with analyzing sulfur in stainless steel, and also incidentally shows the background shift between deionized water and a 5000-ppm metal solution.

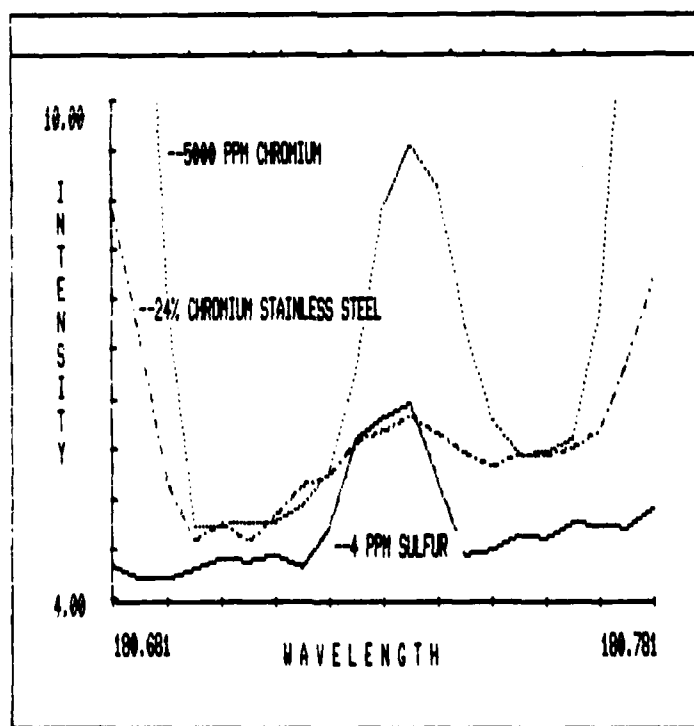


Figure 1. Wavelength scans around the S-180 line.

Table 4. Interference corrections.

Iron Base

<u>Affected Element</u>	<u>Interfering Element</u>	<u>Correction Coefficient</u>
Cr	Mn	0.00033
S	Mn	0.0050
S	Cr	0.00048
Ni	Mn	0.0046
Mn	Mo	0.00026
P	Mo	0.0050
P	Mn	0.0042
Si	Mo	0.0186
V	Mo	0.00016

Aluminum Base

<u>Affected Element</u>	<u>Interfering Element</u>	<u>Correction Coefficient</u>
Zn	Cu	0.0029
Zn	Ni	0.0029

Table 5. Results for iron base standards.

<u>Standard</u>		Al	As	B	Co	Cr	Cu	Mn	Mo	Nb	Ni	P	S	Si	Ta
NBS 361	found	.026	.023	.000	.040	.690	.042	.67	.188	.014	1.935	.017	.014	.22	.014
	certified	.021	.017	.00037	.032	.694	.042	.66	.19	.022	2.00	.014	.0143	.222	.020
		V	Ti	W	Zr										
	found	0.013	.016	.016	.005										
	certified	.011	.020	.017											
NBS 362	found	.074	.101	.001	.303	.296	.496	1.07	.062	.113	.566	.043	.035	.40	.064
	certified	.095	.092	.0025	.30	.30	.50	1.04	.068	.29	.59	.041	.0360	.39	.20
		V	Ti	W	Zr										
	found	0.040	.046	.250	.164										
	certified	.040	.084	.20											
NBS 363	found	.233	.000	.000	.046	1.265	.098	1.50	.026	.022	.301	.0333	.003	.79	.025
	certified	.24	.010	.0078	.048	1.31	.10	1.50	.028	.049	.30	.029	.0068	.74	
		V	Ti	W	Zr										
	found	0.306	.033	.061	.019										
	certified	.31	.050	.046	.049										
NBS 364	found	.011	.055	.008	.151	.059	.251	.26	.476	.043	.143	.015	.026	.07	.020
	certified		.052	.0106	.15	.063	.249	.255	.49	.157	.144	.01	.025	.065	.11
		V	Ti	W	Zr										
	found	0.108	.161	.075	.037										
	certified	.105	.24	.10	.068										
NBS 121	found	.026	As	B	.103	17.15	.127	1.81	.164	.005	11.14	.025	.008	.572	.007
	certified				.10	17.43	.121	1.80	.165		11.17	.019	.013	.54	
		V	Ti	W	Zr										
	found	0.040	.331	.012	.000										
	certified		.342												
NBS 339	found	.013	As	B	.094	17.24	.206	.730	.233	.008	8.79	.116	.014	.482	.009
	certified				.099	17.41	.201	.732	.247		8.87	.135	.013	.652	
		V	Ti	W	Zr										
	found	0.063	.000	.066	.000										
	certified	.058													
NBS 345	found	.009	As	B	.087	15.68	3.45	.218	.123	.158	4.22	.025	.014	.612	.012
	certified				.089	16.04	3.44	.224	.122	.231	4.24	.018	.012	.610	.002
		V	Ti	W	Zr										
	found	0.043	.000	.034	.000										
	certified	.041													

Table 5. Results for iron base standards. (Continued)

Standard		Al	As	B	Co	Cr	Cu	Mn	Mo	Nb	Ni	P	S	Si	Ta
NBS 19	found	0.023			.012	.378	.098	.561	.011	.021	.074	.048	.018	.188	.002
	certified	.031			.012	.374	.093	.554	.013	.026	.066	.046	.033	.186	
	found	V	Ti	W	Zr										
	certified	0.014	.026												
		.012	.027												
NBS 133	found	Al	As	B	Co	Cr	Cu	Mn	Mo	Nb	Ni	P	S	Si	Ta
	certified				.018	12.78 12.63	.086 .080	1.10 1.07	.046 .052		.247 .230	.021 .018	.312 .327	.326 .327	
	found	V	Ti	W	Zr										
	certified	0.060													
		.071													
NBS 72	found	Al	As	B	Co	Cr	Cu	Mn	Mo	Nb	Ni	P	S	Si	Ta
	certified	0.042	.013		.005	.929 .905	.011 .011	.496 .492	.168 .170		.022 .016	.007 .009	.017 .014	.230 .223	
	found	V	Ti	W	Zr										
	certified	0.005	.001												
		.003													
NBS 123	found	Al	As	B	Co	Cr	Cu	Mn	Mo	Nb	Ni	P	S	Si	Ta
	certified	0.031			.136 .12	18.54 17.40	.113 .103	1.81 1.75	.230 .22	.229 .65	11.80 11.34	.030 .024	.012 .014	.581 .59	
	found	V	Ti	W	Zr										
	certified	0.032		.054											
NBS 129	found	Al	As	B	Co	Cr	Cu	Mn	Mo	Nb	Ni	P	S	Si	Ta
	certified				.003	.009 .014	.013 .013	.781 .769	.000 .002		.256 .251	.073 .076	.202 .245	.008 .020	
	found	V	Ti	W	Zr										
	certified	0.012	.001												
		.012													
NBS 367	found	Al	As	B	Co	Cr	Cu	Mn	Mo	Nb	Ni	P	S	Si	Ta
	certified				.024	25.31 24.19	.061	.309 .315	.018		.290 .29	.019 .018	.014 .016	.595 .58	
	found	V	Ti	W	Zr										
	certified	0.086	.001												
		.08													

The accuracy achieved for aluminum, boron, titanium, tantalum, niobium, tungsten and zirconium in iron base was very poor. This is largely attributable to problems in the dissolution process. Titanium, niobium, tantalum, and zirconium all form carbides that are very difficult to dissolve. Treatment of the solutions with perchloric acid, which is sometimes known to dissolve carbides, did not help in this case. Aluminum is sometimes present in steel as acid-insoluble Al_2O_3 , which probably explains the inaccuracies observed. Obviously other dissolution methods need to be explored for these elements. The problem with boron is more complex and requires further investigation.

Table 6 shows the analysis results for five National Bureau of Standards aluminum standards. Standards 855 and 856 are cast aluminums; the other three are wrought aluminums. The values found for most elements were equal to the certified values within experimental uncertainties. An exception to this is silicon, for which the values found were generally low by 5 to 10 percent. This is probably the result of incomplete dissolution of the silicon. In some cases, it is difficult to judge when the hydrogen peroxide treatment has completely dissolved the silicon because the presence of insoluble hydroxides of copper, magnesium, and manganese tends to cloud the basic solution. Still, the recovery of silicon is over 90% with the sodium hydroxide/hydrogen peroxide dissolution method, which is far better than is possible with a HCl/HNO_3 digestion.

Table 7 gives the analysis results for six copper base standards. Four of the standards were from the British Chemical Standards and two were from the National Bureau of Standards. Accuracy is generally not as good as for iron and aluminum base, but for most elements is probably adequate. One problem, noted particularly with BCS 183, was the tendency for tin to precipitate when the sample was dissolved with nitric acid. Probably the tin in the sample was oxidized to tin (IV), which tends to form insoluble precipitates. As an alternative method, a sample of BCS 183 was dissolved in hydrochloric acid and hydrogen peroxide. Hydrogen peroxide is not as strong an oxidizer as nitric acid under acidic conditions, and the soluble tin (II) species is stabilized by the presence of chloride ion. Tin (IV) is less likely to form under these conditions. As noted in table 7, the recovery of tin is much improved by this dissolution method. The recovery of antimony and arsenic is also improved.

Calibration curves were generated with the CSN by using five National Bureau of Standards low-alloy steels. The same analysis wavelengths were used as in the liquid work, with the exception that the 342.20-nm line of titanium was used. This titanium line is on the instrument polychromator. Its use represents a sacrifice of sensitivity for speed of analysis. The standards used were National Bureau of Standards numbers 1261, 1262, 1263, 1264, and 1265. The solid standards 1261, 1262, 1263, and 1264 have the same composition as the chip standards 361, 362, 363, and 364, respectively. Calibration curves were very linear in most cases, an example of which is given in figure 2. Note that raw signal intensities were used to generate these calibration curves. No internal standard was used. Good linear curves were obtained for Al, Nb, Ti, and Zr, indicating that the problem with solution ICP for these elements is definitely in the dissolution process. Calibration curves for B, W, and Ta were either scattered or nonlinear, indicating that the problems observed

Table 6. Results for aluminum base standards.

Standard		Be	Cr	Cu	Fe	Mg	Mn	Ni	Pb	Si	Ti	Zn
NBS 858	found	0.000	.000	.852	.077	1.06	.488	.004		.73	.045	1.06
	certified	.000	.0001	.84	.078	1.01	.48	.0006		.79	.042	1.04
NBS 859	found	.0024	.178	1.603	.20	2.57	.079	.061		.151	.043	5.47
	certified	.0026	.176	1.59	.20	2.45	.078	.063		.17	.041	5.46
NBS 85	found		.203	3.98	.22	1.53	.603	.087	.025	.173	.021	.030
	certified		.211	3.99	.24	1.49	.61	.084	.021	.18	.022	.030
NBS 855	found		.015			.358	.058	.013		6.87	.163	.085
	certified		.013			.37	.057	.015		7.17	.15	.083
NBS 856	found		.057	3.48		.060	.36		.12	8.83	.071	.94
	certified		.055	3.51		.061	.35		.10	9.21	.068	.96

Table 7. Results for copper base standards.

	Cu	Al	As	Mn	Ni	P	Pb	Sn	Fe	Zn	S	Si	Sb
BCS 179	found	57.2	2.42	.011	.836	.615	.029	.33		1.05	32.9		.034
	certified	58.5	2.22		.86	.56		.35		1.02	35.8		.044
BCS 183	found	83.8		.084	.012	1.20	.053	3.06	4.43	.044	3.43	.103	.009
	found*	86.4		.137	.010	1.24	.077	3.19	7.86	.059	3.52		.013
	certified	84.0		.13	.013	1.30	.090	3.15	7.27	.056	3.47	.11	.009
BCS 180	found	66.1			.77	28.7				.74			
	certified	68.1			.75	30.3				.68			
BCS 304	found	80.3			.121	4.59		.004	.02	4.80	.34		.086
	certified	80.2	10.1		.12	4.82		.01	.03	4.64	.31		.08
BCS 871	found	85.6				.090	.00	7.71	.000	.014			
	certified	91.7				.082	.010	8.14	.001	.025			
BCS 872	found	85.3				.16	3.82	5.24	.040	4.07			
	certified	87.4				.26	4.13	4.13	.003	4.0			

* Results from hydrogen peroxide/hydrochloric acid dissolution.

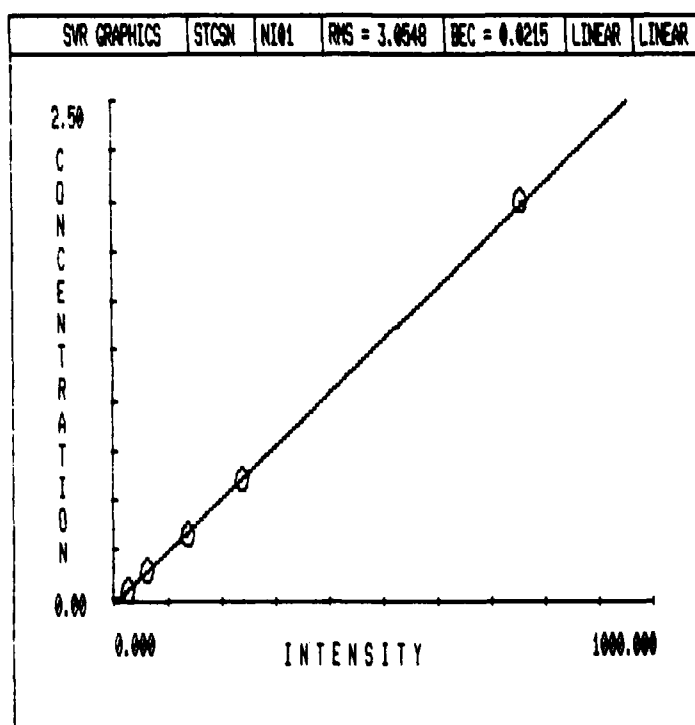


Figure 2. Calibration curve for nickel with CSN-ICP.

in solution ICP may have an origin other than sample dissolution. In general, the CSN introduced about five times as much material into the plasma as the 200-to-1 diluted aqueous samples, providing an increase in sensitivity over solution ICP.

To investigate the possibility of calibrating the spectrometer with liquid multielement standards and then analyzing solid samples by using the CSN as the sample introduction source, the slopes of the calibration curves generated with liquid samples were compared with those generated by solid standards on the CSN. Ideally, one would hope that a single multiplicative factor could be applied to the slopes of all calibration curves to account for the change in the amount of material introduced into the plasma on changing from liquid ICP to CSN-ICP. Table 8 gives the ratios of the slopes of liquid-generated calibration curves to the slopes of CSN-generated curves for those elements for which comparisons could be made. For cobalt, chromium, molybdenum, niobium, vanadium, nickel, and zirconium, the slope ratios agree with a few percent. However, boron, phosphorus, sulfur and copper have significantly different slope ratios. Thus a single correction factor could account for changes in the calibration slope for some but not all of the elements of interest in steel. However, preliminary work by the Applied Research Laboratories suggests that it is possible to calibrate with liquid standards and then use just a few solid standards to correct the calibration curves to run solid unknowns (ref 3).

Some less extensive work was attempted on aluminum base material with the CSN. Calibration curves for Zn, Cu, Si, Be, Mn, Cr, Fe, and Mg were developed by using eight solid standards from the Aluminum Company of America. Calibration curves, with the exception of the Zn calibration curve, were linear. However, in this

Table 8. Ratio of Liquid calibration slopes to CSN slopes.

<u>Element</u>	<u>Slope Ratio</u>
B	357
Co	192
Cr	191
Cu	258
Mo	184
Nb	203
Ni	190
P	281
S	152
V	205
Zr	192

case it was necessary to reference signals to the aluminum signal to get good curves. The calibration curve shown in figure 3 is a plot of relative concentration versus relative intensity. This calibration method accounts for the fact that different amounts of material may be eroded from each sample by the CSN. It was not necessary to use this method on the low-alloy steels.

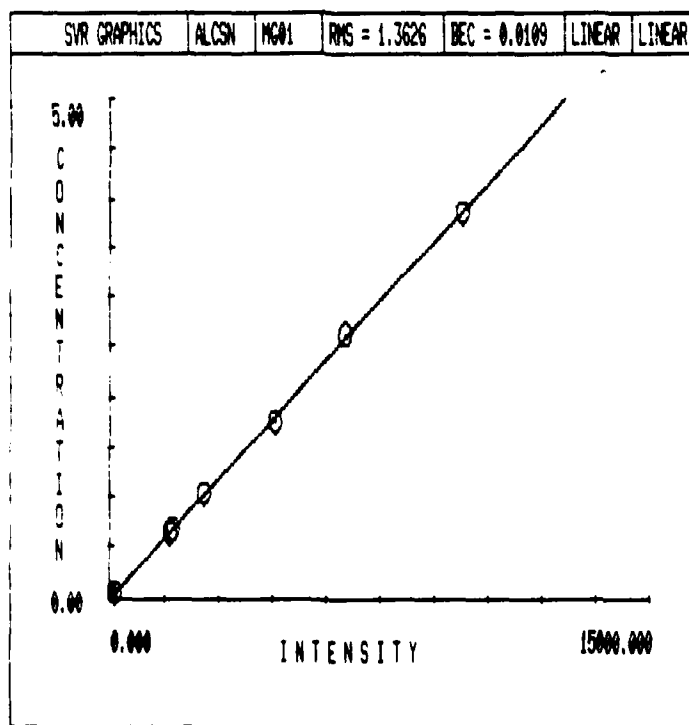


Figure 3. Calibration curve for magnesium with CSN-ICP.

CONCLUSIONS

The analyses of standard reference materials show that the analysis lines given in table 3 are effective for the determination of those elements which can be brought into solution. These lines should give good analytical results when used by any ICP spectrometer with equal or smaller spectral bandpass. The interference corrections of table 4 are bandpass-dependent and will have to be determined separately for spectrometers with bandpasses other than those given in table 3.

The uses of NaOH/H₂O₂ to dissolve aluminum base material and HCl/H₂O₂ to dissolve copper base material show promise as good comprehensive dissolution techniques. Additional research is needed, however, on the dissolution of steels. In particular, methods that release the carbide-forming elements from steel are needed.

The CSN is effective in bypassing the dissolution step, but research must continue into this method's capabilities. In particular, the effectiveness of the CSN for more highly alloyed samples must be examined to determine whether the linearity of calibration curves persists to higher concentrations and to determine whether sample erosion behavior is consistent for highly alloyed material. While it seems that it is not possible to calibrate the system with liquid samples and to analyze solid samples with the CSN by using a single correction factor, it may be possible to use a single solid sample to readjust the calibration curves. If this proves effective, it may be possible to analyze a wide variety of different alloys without purchasing a large number of expensive solid standards.

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